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# Electrical Properties of $Ba_2(In_{1-x}Al_x)_2O_5$ Solid Solutions

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**Abstract**—The electric conductivity of perovskite-like $Ba_2(In_{1-x}Al_x)_2O_5$ solid solutions ($0 < x \le 0.20$) characterized by structural disordering in the oxygen sublattice was studied as a function of temperature and partial pressure of oxygen in an atmosphere with a low content of water vapors ($p_{H_2O} = 3 \times 10^{-5}$ atm). When $In^{3+}$ was partially replaced by $Al^{3+}$, the oxygen ion conductivity increased because of the disordering of oxygen structural vacancies, leading to a significant increase in the total electric conductivity of the samples.

*Keywords*: brownmillerite type, oxygen structural vacancies, disordering effects, oxygen ion conductivity, electron conductivity

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## INTRODUCTION

The introduction of a hetero- or isovalent dopant in the structure of complex oxides is one of the methods of forming and improving their electrical properties. For perovskites $ABO_3$, the introduction of a heterovalent acceptor impurity gives rise to oxygen vacancies and oxygen ion transfer (and, occasionally, to proton transfer) [1]. For perovskite-like phases with a structural disordering such as brownmillerite type oxides $A_2B_2O_5\left[V_O^{\times}\right]_1$ containing large numbers of oxygen structural vacancies $V_O^{\times}$, doping with a donor impurity is used, which leads to growth of conductivity due to a disordering of defects with a partial decrease in their concentration [2, 3]. Isovalent doping is also promising for this class of oxides. An isovalent dopant does not decrease the number of oxygen vacancies, but changes the characteristics of the element–oxygen bond. This makes it possible to control the structural transition temperature and increase the mobility of ionic current carriers [4–7].

Barium indate $Ba_2In_2O_5$ is one of well-defined compounds of brownmillerite type. It exhibits oxygen ion conductivity in an atmosphere with a low content of water vapors and mainly proton conductivity in a wet atmosphere [8–11]. The observed values of conductivity are low because of the ordered arrangement of oxygen vacancies in a brownmillerite structure. The defects are disordered only above 930°C. The symmetry of the structure increases to tetragonal and then to cubic (perovskite type) [12]. Isovalent replacement in the In sublattice, however, can stabilize the disordered structure.

The properties of solid solutions with a composition $Ba_2(In_{1-x}M_x)_2O_5$, where M = $Ga^{3+}$, $Sc^{3+}$, $Y^{3+}$, and $Ln^{3+}$, were described in the literature [4–7]. For substituents with a larger ionic radius compared to that of indium ($Lu^{3+}$, $Yb^{3+}$, $Y^{3+}$, etc.), the structural transition temperature increased; in contrast, for substituents with a smaller radius ($Sc^{3+}$, $Ga^{3+}$), the transition temperature decreased. It was also shown [4] that the total electric conductivity of $Ba_2(In_{1-x}Ga_x)_2O_5$ solid solutions increased with the dopant content compared with the conductivity of undoped barium indate.

Earlier, we showed that the replacement of $In^{3+}$ positions in the structure of $Ba_2In_2O_5$ by the $Al^{3+}$ ion was promising [13]. It was found that the $Ba_2(In_{1-x}Al_x)_2O_5$ samples were monophase in the range $0 < x \le 0.20$ and that the introduction of an isovalent dopant gradually stabilized a disordered structure with a predominantly statistical arrangement of oxygen vacancies. It was also proven that these phases could interact with water molecules, leading to proton defects [13].

Before investigating the evolving proton conductivity and its change in the series of $Ba_2(In_{1-x}Al_x)_2O_5$ solid solutions, it was necessary to study the electric properties of these samples in an atmosphere with a low content of water vapors in the absence of proton transfer. This was the goal of this work.

## EXPERIMENTAL

The $Ba_2(In_{1-x}Al_x)_2O_5$ samples ($0 \le x \le 0.20$) were prepared from $BaCO_3$, $In_2O_3$, and $Al_2O_3$ (ultra high grade) by solid-state synthesis. The synthesis was per-

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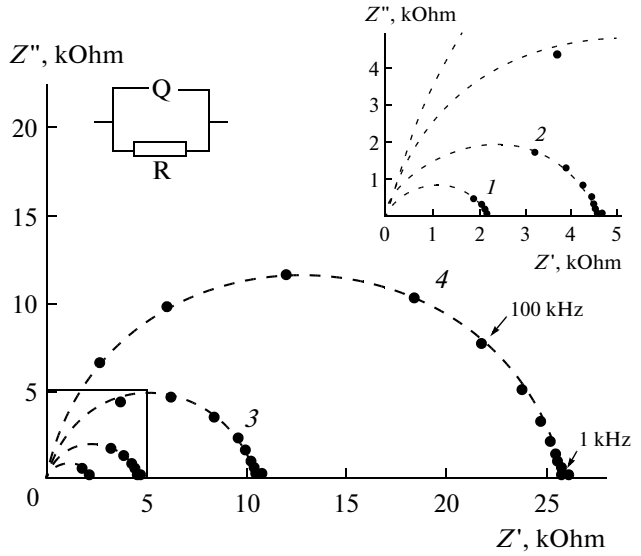


**Fig. 1.** Typical impedance spectra. Data for $x = 0.10$ at temperatures of (*1*) 600, (*2*) 550, (*3*) 500, and (*4*) 450°C.

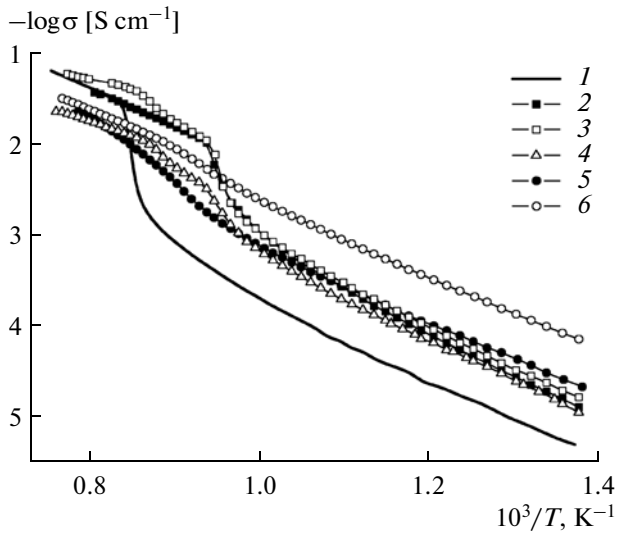


**Fig. 2.** Temperature dependences of the total electric conductivity of $Ba_2(In_{1-x}Al_x)_2O_5$ solid solutions in a dry atmosphere at *x*: (*1*) 0, (*2*) 0.05, (*3*) 0.10, (*4*) 0.13, (*5*) 0.17, and (*6*) 0.20.

formed at 800–1200°C with stepwise heating at a step of 100°C and with isothermal treatments for 10 h. After each synthesis stage, the reaction mixture was ground in an ethanol medium. The samples were molded into cylindrical briquets and additionally annealed at 1300°C for 20 h.

The phase composition of the samples was controlled by X-ray powder diffraction. The X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer ($CuK_\alpha$ radiation, $2\theta = 15°–80°$).

For further studies, porous Pt electrodes were deposited on the end surface of the briquet samples. Electrical measurements were performed by the double contact method on alternating current at $1–10^6$ Hz using an IPI impedance parameter analyzer (the instrument was developed at the Institute of Management Problems, Russian Academy of Sciences, Moscow). The data were interpreted and the sample resistance calculated with the EQUIVCRT program.

The electric measurements were performed while varying the temperature ($T = 450–1000$°C) and partial oxygen pressure ($p_{O_2} = 0.21–1 \times 10^{-16}$ atm). The partial oxygen pressure was set and monitored using electrochemical pump and sensor made from stabilized zirconia $ZrO_2$ (10 mol % $Y_2O_3$).

In the course of the experiment, the partial pressure of water vapors in the measuring cell was maintained low ($p_{H_2O} = 3 \times 10^{-5}$ atm, dry atmosphere) by circulating air preliminarily purified from $CO_2$ through a drying agent ($P_2O_5$ powder or zeolites). The humidity was monitored with a Honeywell HIH-3610 sensor.

The differential scanning calorimetry (DSC) measurements were performed on a NETZSCH STA 409 PC Luxx synchronous thermal analyzer while cooling from 1000 to 600°C at a rate of 10°/min under argon.

## RESULTS AND DISCUSSION

The electric properties of $Ba_2(In_{1-x}Al_x)_2O_5$ solid solutions were studied in a dry atmosphere at 450–1000°C. The concentration of proton defects in the structure of the complex oxide phases under study is negligibly small under these conditions [13] and the ionic component of conductivity, therefore, is mainly determined by the oxygen ion transfer.

Figure 1 presents the typical impedance spectra. On the spectra we can distinguish a semicircle fragment, which probably reflects the overall characteristics of the sample volume and grain boundaries, and a small arc related to the electrode process. Since the contributions from the volume and grain boundary components could not be separated, the sample resistance was taken to be the *R* value obtained in the interpretation of the high-frequency part of the spectrum in accordance with the simple equivalent circuit shown in Fig. 1.

The temperature dependences of the total electric conductivity ($\sigma_{tot}$) of $Ba_2(In_{1-x}Al_x)_2O_5$ solid solutions are presented, together with data for $Ba_2In_2O_5$, in Fig. 2. When a dopant was introduced, the effect of sharply decreased conductivity, resulting from the structural transition from a tetragonal (distorted perovskite) to orthorhombic (brownmillerite) structure, shifted toward lower temperatures and gradually

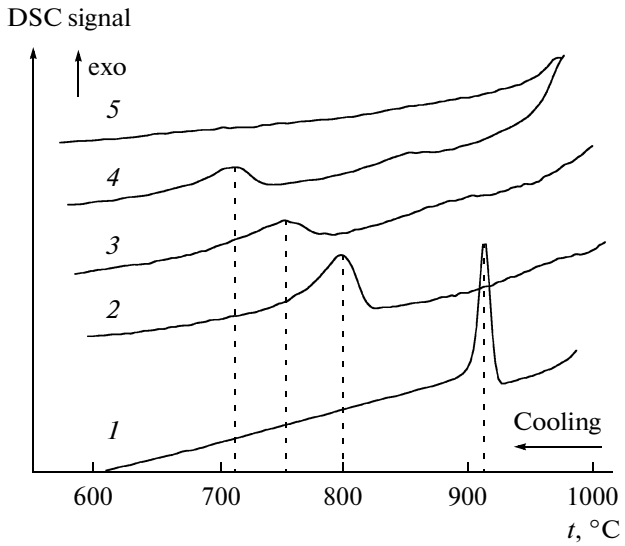


**Fig. 3.** DSC data of studies of $Ba_2(In_{1-x}Al_x)_2O_5$ solid solutions; $x$ = (*1*) 0, (*2*) 0.05, (*3*) 0.10, (*4*) 0.13, and (*5*) 0.20.

smoothed out. For $x = 0.10$ and 0.13, the temperature curve shows another drop of conductivity, which is due to the lowering of structure symmetry from cubic to tetragonal. For $Ba_2In_2O_5$, this transition was observed at 1024°C [12] and thus cannot be seen in the temperature range under study. On the DSC curves, the exothermal effects that characterize the structural transitions also shifted to the low-temperature region as $x$ increased (Fig. 3).

The observed dependence is explained by the stabilization of the structural modification with higher symmetry when the $In^{3+}$ positions were replaced by smaller ions ($Al^{3+}$ in our case) in $Ba_2In_2O_5$. At room temperature, the compositions $Ba_2(In_{1-x}Al_x)_2O_5$ with $x < 0.18$ correspond to the orthorhombic structure with less significant orthorhombic distortions than in barium indate, while the compositions with $x \geq 0.18$ have a tetragonal structure [13].

As is known, $Ba_2In_2O_5$ exhibits mixed ion–electron conductivity in dry atmosphere. The ionic conductivity results from the transfer of oxygen ions and dominates at high temperatures on passing to the tetragonal structure [9]. We can assume that the conductivity of $Ba_2(In_{1-x}Al_x)_2O_5$ is also mixed. To divide the total electric conductivity into ionic and electronic conductivities, $\sigma_{tot}$ was studied as a function of the partial oxygen pressure at 600–900°C. Figure 4 gives the data for $x = 0.16$.

At high $p_{O_2}$, the dependences have a positive slope. Taking into account the effect of $p_{O_2}$ on the concentration of defects in oxides [14], we can state that $p$ type conductivity is considerable in this region. The concentration of hole carriers decreases with the partial oxygen pressure; therefore, the total conductivity of the sample decreases. At medium $p_{O_2}$ values, the atomic defects dominate; this is the region of electrolytic conductivity, which is not affected by the variation of $p_{O_2}$. At higher temperatures, the electrolytic region is expanded, and the slope of the $\log\sigma$–$\log p_{O_2}$ dependences decreases.

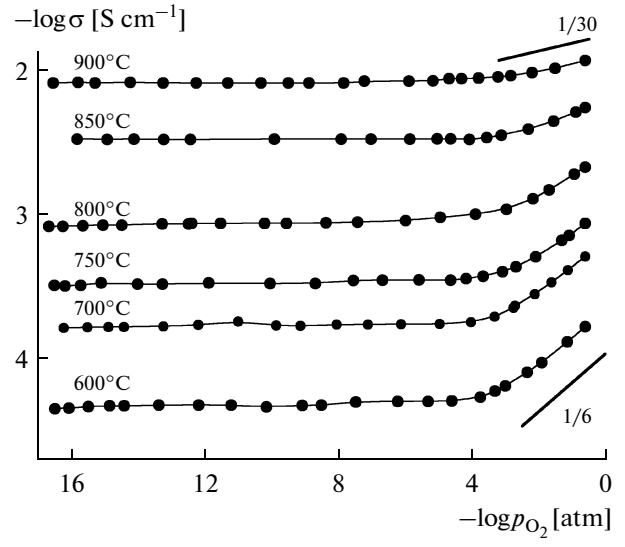


**Fig. 4.** Dependence of the total electric conductivity of the $Ba_2In_{0.68}Al_{0.32}O_5$ sample ($x = 0.16$) on the partial oxygen pressure at different temperatures.

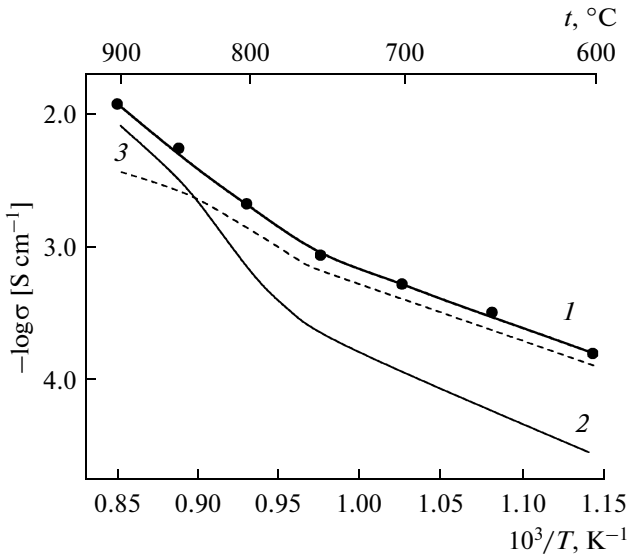


**Fig. 5.** Temperature dependences of the (*1*) total, (*2*) oxygen ion, and (*3*) hole conductivities for the composition with $x = 0.16$.

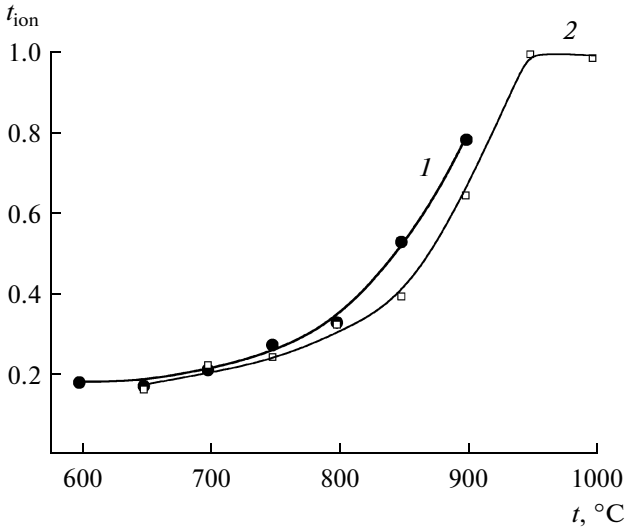


**Fig. 6.** Temperature dependence of the ion transport numbers of the $Ba_2In_{0.68}Al_{0.32}O_5$ sample, $x = 0.16$ (*1*) in comparison with (*2*) the data for $Ba_2In_2O_5$ [7].

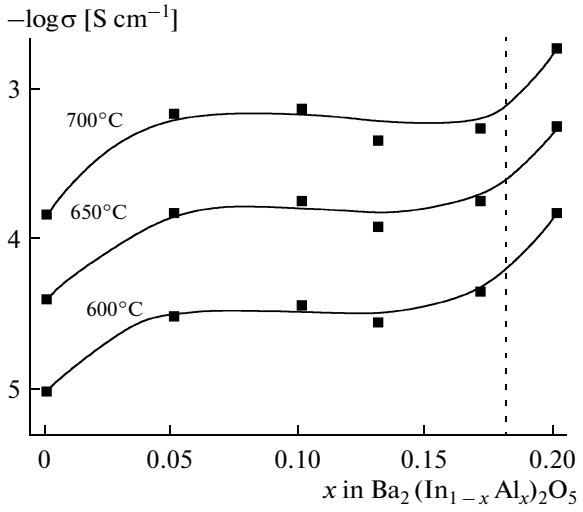


**Fig. 7.** Dependence of the total conductivity on the composition of the solid solution.

Taking into account the structural features of the phases under study, we can argue that in the given range of partial oxygen pressures, the total conductivity consists of ionic ($\sigma_{ion}$) and electron ($\sigma_{el}$) conductivities and can thus be described as [14]

$$\sigma_{tot} = \sigma_{ion} + A(p_{O_2})^{1/4}. \quad (1)$$

An analysis of the experimental data using (1) gave the values of $\sigma_{ion}$ and $\sigma_{el}$. Differentiation of the total conductivity is presented in Fig. 5. Below 750°C the temperature dependences of the oxygen-ion and hole components of conductivity are linear. The apparent activation energies are close: 1.01 and 0.94 eV, respectively. At 750–850°C there is a transition region where the oxygen-ion conductivity significantly increases, which is probably the consequence of the structural transformation. The disordering of oxygen vacancies considerably increases the mobility of current carriers (oxygen ions), leading to growth of $\sigma_{ion}$. The contribution of the oxygen-ion transfer also increases with temperature. The temperature dependences of the calculated ionic transport numbers are given in Fig. 6 in comparison with the literature data for $Ba_2In_2O_5$.

If we consider the temperature range not complicated by structural transitions (below 700°C), the total electric conductivity of $Ba_2(In_{1-x}Al_x)_2O_5$ samples stabilized with small amounts of dopant increases considerably, is then stabilized in a wide range of $x$ (the range of compositions with an orthorhombic structure), and increases again on passing to the sample with a tetragonal structure (Fig. 7). This tendency is also observed for the ionic component of conductivity, which also increases. In the series of compositions, the concentration of oxygen vacancies remains constant. Therefore, growth of ion conductivity results from an increase in the mobility of current carriers.

The electric conductivity of $Ba_2(In_{1-x}Al_x)_2O_5$ solid solutions in dry atmosphere is thus determined by the transport of oxygen ions and *p* type electron carriers. When the oxygen vacancies are disordered with temperature, the fraction and magnitude of the ionic component of conductivity increases. Since isovalent doping also stabilizes the disordered structure, the change in the total conductivity observed in the series of compositions at growing $x$ can be explained by an increase in the ionic component of conductivity due to the higher mobility of oxygen ions.

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